U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-272 763

Multipurpose Gelling Agent and Its Application to Spilled Hazardous Materials

Calspan Corp, Buffalo, N Y

Prepared for

Industrial Environmental Research Lab, Cincinnati, Ohio

Aug 77

PB 272 763

EPA-600/2-77-151
August 1977

Environmental Protection Technology Series

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1 REPORT NO. EPA/600/2-77-151	2 PB272763
4 TITLE AND SUBTITLE: Multipurpose Gelling Agent and its Application to Spilled Hazardous Materials	5 REPORT DATE: August 1977 Issuing date 6 PERFORMING ORGANIZATION CODE
7 AUTHOR(S): J.D. Michalovic, C.E. Akers, R.E. Baier, R.J. Pilie	8 PERFORMING ORGANIZATION REPORT NO
9 PERFORMING ORGANIZATION NAME AND ADDRESS: Calspan Corporation, Buffalo, New York 14221	10 PROGRAM ELEMENT NO: 1BB610 11 CONTRACT/GRANT NO: 68-03-2091
12 SPONSORING AGENCY NAME AND ADDRESS: Industrial Environmental Research Lab. - Cin., OH, Office of Research & Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268	13 TYPE OF REPORT AND PERIOD COVERED: Final Report 14 SPONSORING AGENCY CODE: EPA/600/12
15 SUPPLEMENTARY NOTES:	

16 ABSTRACT

Previously, a blend of materials was formulated that would spontaneously gel a wide variety of hazardous liquids. This blend, known as the Multipurpose Gelling Agent (MGA), has been optimized to obtain a balanced formulation that will effectively gel and immobilize most spilled hazardous liquids within minutes. The current formulation, consisting of four powdered polymers and one inorganic powder, has the ability to immobilize spilled liquids with the least amount of material in the shortest period of time. In field testing of the powdered blend, it was observed that when air conveyance modes of dispersal were employed high losses occurred due to the effects of wind. Three compressed and granulated forms of the gelling agent were developed which are clearly superior to the original powdered blend for delivery to liquid spill targets. Various off-the-shelf dry solid dispersion devices were evaluated and the most promising systems field tested on simulated and actual spill targets, both in pools and in linear ditches. The results show that MGA provides an efficient means to mitigate the damages from hazardous liquid spills.

17 KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Hazardous Materials, Gelling Agents, Gelation, Dispensers, Decontamination	Hazardous Materials Spills Clean-up Hazardous Material Spill Control Multipurpose Gelling Agent	13B

18 DISTRIBUTION STATEMENT: Release to Public	19 SECURITY CLASS (This Report): Unclassified	21 NO. OF PAGES: 87
	20 SECURITY CLASS (This page): Unclassified	22 PRICE: A04 - A01

EPA Form 2220-1 (9-73)

EPA-600/2-77-151
August 1977

MULTIPURPOSE GELLING AGENT AND ITS APPLICATION TO SPILLED HAZARDOUS MATERIALS

by

J. G. Michalovic
C. K. Akers
R. E. Baier
R. J. Pilie
Calspan Corporation
Buffalo, New York 14221

Contract No. 68-03-2091

Project Officer

Joseph P. Laforgnta
Oil and Hazardous Materials Spills Branch
Industrial Environmental Research Laboratory-Cincinnati
Edison, New Jersey 08817

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory-Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. It documents the laboratory and field studies conducted to determine the optimum formulation, and dispersal means for a multipurpose gelling agent for immobilizing hazardous material spills on land. As such it serves as a reference to those in state, local and Federal Agencies and the transportation and chemical industries, and others who are interested in the control of spills of hazardous materials. This project is part of a continuing program of the Oil and Hazardous Materials Spills Branch, IERL-Ci to assess and mitigate the environmental impact of pollution from hazardous material spills.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Under contract to the U. S. Environmental Protection Agency, a blend of materials was formulated that would spontaneously gel a wide variety of hazardous liquids. This blend, known as the Multipurpose Gelling Agent (MGA), has been optimized to obtain a balanced formulation that will effectively gel and immobilize most spilled hazardous liquids within minutes. The current formulation, consisting of four powdered polymers and one inorganic powder, has the ability to immobilize spilled liquids with the least amount of material in the shortest period of time, but evaluations of alternate materials are still in progress. In field testing of the blend, it was determined that air conveyance modes of dispersal could be employed but with high losses due to the effects of wind on the powdered form. Three compressed and granulated forms of the gelling agent were then developed which are clearly superior to the original powdery blend for delivery to liquid spill targets. Various off-the-shelf dry solid dispersion devices were evaluated and the most promising systems field tested on simulated and actual spill targets, both in pools and in linear ditches. The results show that MGA provides a potentially cost-effective and efficient means to mitigate the damages from hazardous liquid spills.

This report was submitted in fulfillment of Contract No. 68-03-2093 by Calspan Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from 28 June 1974 to 28 August 1975, and work with technical effort was completed as of 28 July 1975.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables viii

I. Introduction 1
II. Summary, Conclusions and Recommendations 2
Summary and Conclusions 2
Recommendations 3
III. Laboratory Optimization of the Multipurpose Gelling Agent (MGA) 4
Background 4
Gelling Agent Blend Optimization 6
Cost of MGA 11
Substitute Gelling Agent Materials 13
Storage Requirements 16
Preliminary Bioassay 17
Procurement and Physical Specifications 17
IV. Physical Form of Gelling Agent 20
Background 20
Optimization of MGA Physical Form 22
Forms Tested 22
Summary of Test Results 22
Detailed Test Results 24
Powder form 24
Agglomerate form 24
Tablet form 24
Graded form 27
Webbed form 27
Mat form 29
Roll compressed form 29
Spun polyolefin bag evaluation 30
V. Dispersal of the MGA 31
Background 31
Dissemination Systems Evaluations 33
Pressurized Tank 33
Venturi/Compressed Air 34
Centrifugal Blower 36
Auger-Fed/Pneumatic Conveyor 36
Nozzle Configuration 40
Mass Distributions of Powdered MGA 40
VI. Discussion 45

FIGURES

Number		Page
IV-1	Effect of wind on powdered form of MGA being dispersed	21
IV-2a	"Graded" form of MGA	28
IV-2b	"Graded" form of MGA (SEM, 20 KV, 40° tilt, 10X mag.)	28
V-1a	Venturi tube - compressed air nozzle	35
V-1b	Diagram of Airplace Econo-Vac nozzle	35
V-2	Venturi compressed air system blowing powdered form MGA	37
V-3	Long tube on Venturi-compressor	38
V-3a	Dispersing agglomerated form	38
V-3b	Gelled trichloroethane	38
V-4	Centrifugal blower (snowblower)	39
V-4a	Experimental apparatus	39
V-4b	Blowing powdered MGA	39
V-5	MGA dispersed from pneumatic-conveyor/auger-fed system Powdered MGA being dispersed from 30-meter (100-foot) hose	41
V-6	Equal mass distribution contour map obtained from CO_2-charged dry chemical fire extinguisher dispersion of MGA	42
V-7	Mass distribution of MGA dispersed from CO_2-charged dry chemical fire extinguisher	44

TABLES

Number		Page
III-1	Compounds Tested with MGA	6
III-2	Minimum Amount of Gelling Agent Required to Form an Immobile Gel (g/10 ml)	7
III-3	Effectiveness of Gelling Agent Blends	8
III-4	Formulation of MGA Blends	10
III-5	Amount of Blend Required for Gelling Alcohols	10
III-6	Hydroxypropyl Cellulose [Klucel (Hercules)] Gelling Qualities (g/10 ml)	11
III-7	Cost Per Pound (Per Kilogram) of Gelling Agent Blends C, D, E	12
III-8	Potential Substitute Materials Considered	14
III-9	Physical Properties of MGA Components	18
III-10	Classification of MGA Components	19
IV-1	Test Liquids	23
IV-2	Efficiency of Physical Forms of MGA	25
IV-3	Gelling Efficiency of Powder MGA (Blends D & E)	26
V-1	Dispersion Devices	32

SECTION I

INTRODUCTION

The purpose of this investigation was to develop materials and equipment which could be used to gel and, thereby, immobilize a wide variety of liquid chemical compounds that may be spilled to the detriment of the environment.

The ideal countermeasure to any spill of a hazardous material is to terminate the spill as soon as possible by sealing the material in its original container. Once hazardous chemicals are on the ground, the most attractive secondary countermeasure consists of immobilization of the chemical to minimize the affected land area, to prevent flow of hazardous liquids to surface water, and to minimize percolation of liquids into the surface and subsoils. Immobilization of a spilled liquid with a gelling agent ideally leaves the material in a form that can be easily removed by mechanical means.

Under an earlier EPA sponsored program on "Methods to Treat, Control and Monitor Spilled Hazardous Materials" (Contract No. 68-01-0110)* a preliminary blend of materials was formulated that was useful for gelling both organic and inorganic liquids. The mixture was tested on 35 hazardous chemical compounds that were successfully gelled. This original blend, because of its ability to thicken and gel all hazardous liquids tested, was referred to as the "Multipurpose Gelling Agent" (MGA).

The first objective of this study was to determine the gelling agent formulation which would provide an optimum balance of gelling speed, ease of application and product cost. Generic components and suitable generic substitutes were identified as far as possible. The requirements for storage were identified and are reported herein. Consideration was also given to the physical form of the agent to make it more amenable to effective delivery to an interaction with a spilled liquid. Various physical forms of the MGA were evaluated with respect to gelling efficiency and ease of dispersion.

The second objective was to evaluate various types of dry dissemination devices that would be suitable for dispensing the gelling agent in a spill situation. Consideration was given only to "off-the-shelf" equipment. The types of devices showing the most promising principles of operation were field tested on simulated spill targets to define dispersion, delivery capacity, rate of delivery, portability, and unit cost.

*This work was carried out under contract to the Environmental Protection Agency, Edison, N.J. from 29 June 1971 to 27 November 1972.

SECTION II

SUMMARY, CONCLUSIONS & RECOMMENDATIONS

SUMMARY & CONCLUSIONS

The MGA developed under EPA Contract Number 68-01-0110, "Methods to Treat, Control and Monitor Spilled Hazardous Materials," was optimized to obtain a balanced formulation that would effectively gel a large variety of spilled hazardous liquids.

A formulation, Blend B, consisting of a polyacrylamide, a polytertiary-butylstyrene, a polyacrylonitrile rubber, a polycarboxymethyl cellulose, and a fumed silica was determined to be the optimum gelling agent based on its ability to immobilize the greatest variety of hazardous spill liquids with the least amount of material.

Also evaluated were alternate materials that could possibly be substituted for components of the MGA. Commercial sources for each of the ingredients were identified and preliminary generic descriptions obtained.

It was determined through early field testing that the powder form of the MGA could be deployed using air conveyance modes of dispersal but only with high losses due to effects of wind. Three compressed and granulated forms of the MGA were developed which are clearly superior to the original powdery blend for field dispersal onto liquid spill targets.

Various off-the-shelf dry solid dispersal devices were evaluated with the most promising dispersal modes field tested. Auger-fed, pneumatic-conveyor systems ("Rockduster") originally developed for the coal mining industry were shown to be best suited for distribution of MGA at high rates and acceptable accuracy. The portable "sandblaster" was also found to be an acceptable delivery device.

Delivery nozzles bent at 30° to the horizontal plane of the dispersing tube provide better accuracy and agent distribution than straight-pipe nozzles.

Using 1975 quotations for raw materials, preparation and packaging, it was estimated that large quantities of MGA may be prepared in granular form for between $4.40 and $5.50 per kilogram ($2.00 and $2.50 per pound).

The MGA must be stored in moisture-proof containers at temperatures less than 50°C (122°F).

A ten-minute film was produced showing the various tested dispersion devices, various physical forms of the agent, and the gelling of a test chemical.

RECOMMENDATIONS

The MGA is now sufficiently well-defined to be manufactured and stored in reasonably large batches. It is recommended that approximately 1350 kilograms (3000 pounds) of this material be procured and utilized in large-scale field experiments to more completely demonstrate its efficacy.

Smaller scale tests should be run with MGA forms produced by a variety of manufacturing techniques so that the optimum physical characteristics for both dispersal and gelling efficiency may be defined. Commercially available substitute ingredients should be incorporated into small MGA batches, averaging 45 kilograms (100 pounds) or so, to guarantee their suitability for free substitution as market and/or material conditions dictate.

Auger-fed, pneumatic-conveyor systems should be obtained and field-tested, followed by redesign, if necessary, for MGA distribution to large spill targets.

Ultimate clean-up measures to be applied following successful use of the MGA should be experimentally determined, and the prospects for economical recovery of the spilled liquid from the containing gel mass should be investigated.

SECTION III

LABORATORY OPTIMIZATION OF THE MGA

BACKGROUND

Under a completed EPA sponsored research program on "Methods to Treat, Control, and Monitor Spilled Hazardous Materials" (Contract No. 68-01-0110), Calspan developed and evaluated a mixture of several dry chemical materials for immobilizing spills of hazardous liquid chemical substances. The hazardous liquid chemicals considered in that program are listed in Table III-1. They were selected for study on the basis of toxicity, volumes shipped, and previous histories of spills.

There were a number of criteria used in the development of the MGA. One was that the gelling agent should be able to immobilize a broad spectrum of organic and inorganic liquids. The development of many specific agents would create a perhaps insurmountable logistics problem. A second criterion was that the presence of, or interaction of, the treatment agent should not create a serious secondary hazard, such as increased danger of fire or explosion.

The MGA developed represented a new composition of matter, created by the mechanical blending of equal weights of five specific components having the following properties.

The first component was a material of the highly water-soluble polyelectrolyte-type, typified by polyacrylamide. This material was selected for its ability to thicken water and aqueous solutions.

The second component of the blend was a loosely crosslinked copolymer of the class typified by polytertiary-butylstyrene copolymerized with divinylbenzene. This material was selected to interact most strongly with those liquids having almost no polarity and only poor solvent power such as cyclohexane, gasoline fractions, and a variety of other inert spirits.

A third component was a material of the polyacrylonitrile-butadiene copolymer class chosen to be especially effective against the very strongly polar organic chemicals such as acrylonitrile, ethylene dichloride, and other chlorinated or polar liquids.

The fourth required component of the blend was a material to cope with the most difficult of all hazardous liquids to thicken, solidify, and immobilize in place, as typified by methyl alcohol and other chemicals of the alcoholic class. Materials suitable for this use included the polycarboxymethylcellulose polymers.

TABLE III-1. COMPOUNDS TESTED WITH THE MOA

ACETONE	FORMALDEHYDE
ACETONE CYANOHYDRIN	GASOLINE
ACRYLONITRILE	ISOPRENE
AMMONIUM HYDROXIDE	ISOPROPYL ALCOHOL
ANILINE	KEROSENE
BENZALDEHYDE	METHANOL
BENZENE	METHYL ETHYL KETONE
BUTANOL	OCTANE (2,2,4 TRIMETHYL PENTANE)
CARBON DISULFIDE	ORTHO-DICHLOROBENZENE
CARBON TETRACHLORIDE	PETROLEUM ETHER
CHLORINE WATER (SATURATED)	PHENOL (80%)
CHLOROFORM	PYRIDINE
CYCLOHEXANE	SULFURIC ACID
CYCLOHEXANONE	TETRAHYDROFURAN
ETHANOL	TRICHLOROETHYLENE
ETHYL ACETATE	WATER
ETHYLENE DICHLORIDE	XYLENE
ETHYLENE GLYCOL	

This four-component blend uses the commercial products with the following trade names:

(1) Gelgard, Dow Chemical Corporation, to combat spills of aqueous liquids;

(2) Imbiber Beads, Dow Chemical Corporation, to combat spills of the inert spirits-type liquids;

(3) Hycar 1472, BF Goodrich Corporation, to combat the polar organic chemical spills including the chlorinated hydrocarbons; and

(4) Carbopol 934, BF Goodrich Corporation, to combat spills of alcoholic liquids.

For ease of delivery of this four-polymer blend, it required fluidization to ensure rapid, smooth egress from commercial spray equipment. Addition of fumed silica (e.g., Cabosil, Cabot Corporation) was used.

GELLING AGENT BLEND OPTIMIZATION

The four powdered polymers, each capable of congealing at least one class of hazardous liquid into an immobile mass, were originally selected and combined in equal parts by weight and fluidized with fumed silica to form MGA.

To achieve an optimum blend, the proper proportioning of the above components had to be pursued. A number of laboratory tests were performed to obtain a formulation which would minimize material cost without sacrificing the effectiveness against a broad spectrum of spills. Each test liquid was treated with individual gelling agent components to ascertain the least practical amount of material required to congeal specific fluids into immobile gels. Also, a mixture of equal amounts (20% by weight) of each polymer and fumed silica was added to each of the test liquids.

The amount of each polymer and of the mixture necessary to gel a liquid was determined by adding small amounts of polymer to 10 ml of liquid in a 3-inch aluminum pan. When the aluminum pan could be inverted without loss of the gelled fluid the exact weight of polymer added was recorded. Table III-2 lists the experimental results.

It is apparent from Table III-2 that in all cases the mass of the blend required to congeal the test liquids is less than five times the mass of the specific active agent required to produce the same results. The ingredients of the blend did not act independently. In all cases, a degree of synergism exists which is associated, at least in part, with physical "sopping" of the test liquid by nonactive components of the blend.

TABLE III-2. MINIMUM AMOUNT OF GELLING AGENT REQUIRED TO FORM AN IMMOBILE GEL (g/10ml)

10 ml	Geigard (g)	Imbiber Beads (g)	1422 Hycar (2% Cabosil) (g)	Carbopol (g)	Blend A* (g)
Acetone	#	#	0.58	1.38	1.15
Acetone Cyanohydrin	11.68	#	1.25	2.64	2.11
Acrylonitrile	5.47	4.21	0.58	1.43	1.25
Ammonium Hydroxide	0.22	#	#	#	0.32
Aniline	#	#	0.72	#	1.47
Benzaldehyde	#	2.05	0.54	#	1.07
Benzene	#	0.58	0.54	#	0.50
Butanol	#	#	#	0.74	2.47
Carbon Disulfide	7.56	0.70	2.50	#	1.25
Carbon Tetrachloride	#	0.42	#	1.11	1.20
Chlorine Water	0.14	#	#	#	0.47
Chloroform	#	0.47	0.33	#	0.76
Cyclohexane	#	0.95	#	#	1.13
Cyclohexanone	#	2.52	0.54	#	1.35
Ethanol	#	#	#	0.52	0.98
Ethyl Acetate	#	0.80	0.72	#	1.05
Ethylene Dichloride	#	1.10	0.43	#	1.05
Ethylene Glycol	4.32	#	#	0.67	0.78
Formaldehyde	0.58	#	#	0.74	0.52
Gasoline	#	0.74	3.62	#	1.27
Isoprene	#	0.42	1.52	#	0.83
Isopropyl Alcohol	#	#	#	1.11	2.38
Kerosene	#	2.37	6.11	#	2.15
Methanol	#	#	#	0.57	1.05
Methyl Ethyl Ketone	#	0.84	0.54	#	1.15
Octane	#	4.05	#	1.01	1.80
O-Dichlorobenzene	#	0.74	0.51	#	1.08
Petroleum Ether	5.74	0.58	2.17	#	1.03
Phenol	#	#	0.54	1.80	1.20
Pyridine	#	1.58	0.51	#	1.03
Sulfuric Acid	1.22	#	1.45	#	0.98
Tetrahydrofuran	#	0.68	0.47	0.84	0.76
Tetrachloroethylene	#	0.65	0.47	#	0.81
Water	0.07	#	#	#	0.12
Xylene	#	0.74	1.00	#	1.18

* 20% of each of: Geigard, Imbiber Beads, Hycar (2% Cabosil), Carbopol, and Cabosil.

\# No gel formed.

With these data available, the relative proportions of the five ingredients were modified in subsequent mixtures in an attempt to produce a blend which could be used to treat all of the test chemicals with the same dosage. An arbitrary goal of one gram or less of the gelling agent per 10 ml of liquid was established.

Based on inspection of the data presented in Table III-2, Blends B and C were prepared and tested with the same 58 representative chemical compounds that had been used earlier. Table III-3 compares Blend B and C with the original, equally proportioned blend (Blend A). Formulations of these blends are listed in Table III-4.

From Table III-3 it is apparent that Blend B is inferior to Blend A, in terms of mass agent required, for 19 of the 28 cases in which both were tested. Blend C, however, is superior to Blend A in this respect for 25 of the 58 comparisons made. Furthermore, where C is not clearly superior to A, the difference in mass requirements is, in each case, relatively minor.

If the amount of gelling agent from each blend tested is summed and divided by the number of measurements, a numerical comparison can be made among Blends A, B and C. The average amount of Blend A to gel 10 ml of liquid is 1.15g. The amounts of Blends B and C are 1.48 and 0.91g, respectively. This clearly shows the effectiveness of Blend C over Blends A and B.

Note that in most cases the arbitrarily established goal of 1.0g of agent per 10 ml of test liquid was achieved in Blend C. There are, however, some chemical compounds, such as acetone cyanohydrin, isopropyl alcohol, butanol, and octane, which required approximately twice that dosage rate for gelation. These deviations from the goal suggested that further mixture adjustments be made to enhance the gelling efficiency for alcohols. The Carbopol concentration in Blend C was, therefore, increased, and the Hycar concentration decreased to form Blend D. Results obtained with alcohols are presented in Table III-5. Within the accuracy of the experiments, tests of each of the other three gelling agent ingredients indicated no change in dosage requirement relative to Blend C.

Blend D was, therefore, selected as the principal mixture to be used in experiments pertaining to control of physical characteristics of the gelling agent and testing of dissemination equipment. Orders were placed for sufficient quantities to perform these experiments. Subsequently experiments were performed on substitute gelling agent materials which led to Blend E described below.

A substitute material which has potential for the immobilization of alcohols, the most difficult of all hazardous liquids to gel, was evaluated. Klucel is a hydroxypropyl cellulose, nonionic, water-soluble cellulose ether. Klucels M and H both have the same structure, with M having a higher molecular weight. Table III-6 lists data which show these materials to be superior to Carbopol 934 in gelling the low-molecular-weight alcohols. In addition, the gels formed with the Klucel were more elastic and possessed greater coherence.

TABLE III 5 EFFECTIVENESS OF GELLING AGENT BLENDS A, B, AND C
(g/10ml OF CHEMICAL REQUIRED FOR GELATION)

Chemical (10 ml)	Blend A (g)	Blend B (g)	Blend C (g)
Acetone	1.10	1.20	0.95
Acetone cyanohydrin	2.11	3.05	2.23
Acrylonitrile	1.20	1.75	1.11
Ammonium hydroxide	0.32	0.35	0.31
Aniline	1.45	1.11	0.95
Benzaldehyde	1.57	1.23	0.82
Benzene	0.50	1.12	0.30
Butanol	1.47	1.50	2.07
Carbon disulfide	1.23	1.35	0.58
Carbon tetrachloride	1.20	1.30	0.71
Chlorine water	0.47	0.35	0.61
Chloroform	0.76	0.60	0.45
Cyclohexane	1.13	1.26	0.93
Cyclohexanone	1.35	1.10	0.75
Ethanol	0.08	1.75	1.33
Ethyl Acetate	1.05	1.23	0.86
Ethylene Dichloride	1.03	0.95	0.53
Ethylene Glycol	0.78	2.82	1.03
Formaldehyde	0.52	0.75	0.60
Gasoline	1.27	1.10	0.90
Isoprene	0.83	1.30	0.71
Isopropyl Alcohol	2.38	1.73	2.15
Kerosene	2.10	1.80	1.30
Methanol	1.03	1.65	1.14
Methyl Ethyl Ketone	1.13	0.88	0.72
Octane	1.30	*	1.00
O-Dichlorobenzene	1.08	*	0.60
Petroleum Ether	1.03	*	0.80
Phenol	1.20	1.30	0.80
Pyridine	1.03	*	0.61
Sulfuric Acid	0.38	*	0.08
Tetrahydrofuran	0.76	*	0.37
Trichloroethylene	0.81	*	0.50
Water	0.12	0.75	0.48
Xylene	1.18	1.12	0.60

*Not tested.

TABLE III 4. FORMULATION OF MGA BLENDS (% BY WEIGHT)

Blend	Celgard	Imbiber Beads	Hyear	Carbopol	Cabosil	Klucel H
A	20	20	20	20	20	*
B	15	30	35	15	5	*
C	5	30	35	20	10	*
D	5	30	30	25	10	*
E	5	35	20	*	10	30

*Not used.

TABLE III 5. AMOUNT OF BLEND REQUIRED TO GEL ALCOHOLS

	BLEND (g)	
Liquid (10 ml)	C	D
Methanol	1.14	0.92
Ethanol	1.33	1.17
Isopropanol	2.15	1.47
1 - Butanol	2.60	2.21

TABLE III-6. GELLING QUALITIES OF HYDROXYPROPYL CELLULOSE (KLUCEL M AND KLUCEL H) AND CARBOPOL 934 (g/10ml)

	Klucel M	Klucel H	Carbopol 934
Acetone	0.81	0.66	1.38
Acetone cyanohydrin	1.39	1.25	2.64
Acrylonitrile	1.15	1.22	1.45
Butanol	1.02	0.80	0.74
Ethanol	0.95	0.70	0.52
Ethylene glycol	2.27	2.27	0.67
Isopropyl alcohol	1.02	1.02	1.11
Methanol	0.88	0.70	0.57
Phenol (80%)	1.20	1.18	1.80

Klucel H was incorporated into Blend D as a substitute for Carbopol later in this study (Blend E). This blend was tested for dosage requirements and gelling speed. As indicated in Table IV-3, Blend E is slightly superior to Blend D. The overall advantages, however, were not considered to be so important as to warrant repetition of packaging and dissemination experiments performed with Blend D.

COST OF MGA

A preliminary cost analysis of the MGA is based upon the costs of ordering and producing 450-kg (1000-lb) batches of agent. The cost per pound will decrease as the quantity of material ordered increases. This reduction in cost, however, is not expected to exceed 15 to 20%. The cost of Blends C, D (standard MGA formulation), and E are given in Table III-7. Costs given reflect only the price per pound of the base materials. The cost for blending, forming, and packaging is not included in Table III-7. For a 450-kg (1000-lb) batch, the cost for blending is $0.55/kg ($0.25/lb) and packaging $0.22/kg ($0.10/lb). The cost for preparation of a special form (i.e., pressing, rolling, chipping) is not included because no such processing has yet been done with large lots. These costs, however, would not be expected to increase the price above $0.55/kg ($0.25/lb). Final costs of the gelling agent would be expected to be in the $4.40 to $5.50/kg ($2.00 to $2.50/lb) range. These costs reflect 1975 economic conditions and are substantially higher than our 1973 estimates of $1.10/kg ($0.50/lb). If current economic trends continue, the cost per pound of gelling agent is expected to increase further.

TABLE III-7. COST PER POUND (PER KILOGRAM) OF GELLING AGENT BLENDS C, W, E

	Blend C			Blend D			Blend E		
	%	$/lb ($/kg)	$	%	$/lb ($/kg)	$	%	$/lb ($/kg)	$
Gelgard	5	2.65 (4.51)	0.1325 (0.1355)	5	2.65 (4.51)	0.1325 (0.1355)	5	2.65 (4.51)	0.1325 (0.1355)
Imbiher Beads	30	2.87 (6.31)	0.9610 (1.8930)	30	2.87 (6.31)	0.8610 (1.8952)	30	2.87 (6.31)	1.8145 (1.8934)
Dycar 1411	35	0.71 (1.56)	0.2485 (0.5460)	30	0.71 (1.56)	0.2130 (0.4680)	20	0.71 (1.56)	0.1420 (0.3120)
Cathopal 954	20	2.50 (5.50)	0.5000 (1.1000)	25	2.50 (5.50)	0.6250 (1.3750)	*	—	—
Klucel H	*	—	—	*	—	—	30	2.35 (5.17)	0.7050 (1.5510)
Cabosil	10	1.76 (3.87)	0.1760 (0.3870)	10	1.76 (3.87)	0.1760 (0.3870)	10	1.76 (3.87)	0.1760 (0.3870)
$/lb ($/kg) of Blend			1.8880 (4.1536)			1.9775 (4.3505)			2.1480 (4.7256)

*Not used.

It should be noted that since the start of this work, the manufacture of Gelgard M has been discontinued by the Dow Chemical Corporation. Small supplies of Gelgard are still available, and Dow will resume manufacture if an order is sufficiently large. Substitute material has also been found that works similarly to Gelgard. This material (Kelsan) is discussed with other potential substitute materials in the next section.

SUBSTITUTE GELLING AGENT MATERIALS

In order to broaden the scope and universality of the gelling agent, a search for substitute gelling agent materials was performed. Manufacturers of gelling and thickening compounds were contacted and products obtained for laboratory evaluation (Table III-8).

The materials were evaluated against the following criteria:

(1) - Material must be a dry powder with low moisture content.

(2) - Material must form viscous gels without extreme stirring or heating.

(3) - Material gelling efficiency must compare directly with current MEA components.

Each of the potential substitute materials was screened using these representative liquids from the four major chemical classes:

Class I	- liquids (aqueous solutions)	Water
Class II	- liquids (nonpolar organics)	Cyclohexane/Isooctane
Class III	- liquids (polar organics)	Trichloroethane
Class IV	- liquids (alcohols)	Methanol

Specific Product Evaluations

Pluronic F-127 (BASF Wyandotte Corporation)--The literature on Pluronic F-127 (polyoxyethylene and polyoxypropylene) states that two techniques have been developed for preparing Pluronic gels -- one based on cooling a hot solution; the other on warming a cool solution. Neither of these techniques is applicable to our specific problem.

When Pluronic F-127 was added to various liquids (at ambient temperature) no thickening occurred. This product was rejected as a candidate material.

Alcogum L-11 (Alco Chemical Corporation)--This thickener is supplied in liquid form. It was rejected as a substitute material.

Stearates (Witco Chemical Organics Division)--Stearate gels are formed by heating a solution of stearates plus the solvent to be thickened and then

TABLE III-8. POTENTIAL SUBSTITUTE MATERIALS CONSIDERED

Company	Trademark	Generic Name	Class			
			I	II	III	IV
GAF	Gantrez AS	Poly (methyl vinyl ether maleic anhydride)	x		x	x
	PVP	Polyvinylpyrrolidone	x			
Union Carbide	Polyox	Ethylene oxide polymer	x			
	Cellosize	Hydroxyethyl cellulose	x			
Alco Chem.	Alcogum L-11	Polyacrylate	x	x		
BASF	Pluronic F 127	Mix of poly(oxypropylene) and poly (oxyethylene)	x		x	x
Kelco	Kelzan	Xanthan gum	x		x	x
	Solvid	Gum		x	x	x
Drycal Chem.	Gum	Gum	x			x
Witco	Metallic soap	Aluminum stearate		x		
		Aluminum palmitate		x		
		Aluminum octoate			x	
B.F.Goodrich	K-718	Polyacrylate	x			
	Carbopol 940	Polyacrylate	x	x		
Hercules	Klucel	Hydroxypropyl cellulose	x		x	x

Class I - Aqueous Solutions
II - Nonpolar Organics
III - Polar organic
IV - Alcohols

cooling the mixture in a stepwise manner. This product was rejected as a candidate material.

Gantrez-AN (GAF, Dyestuff and Chemical Division)--Four Gantrez-AN samples were received for evaluation (Gantrez-AN, 119, 139, 149, 169). The literature stated that a slurry of Gantrez-AN should first be prepared at 95-99°C. After 10 to 20 minutes of high speed stirring, the slurry would become viscous. When Gantrez-AN was evaluated using our laboratory procedure, no thickening occurred. Therefore, the product was rejected as a substitute material.

PVP (GAF, Dyestuff and Chemical Division)--Polyvinylpyrolidone did not perform well as a thickening agent under our evaluation procedure. It was rejected as a substitute material.

Soloid (Kelco Company)--The commercial development data sheet states that "Soloid is a new solvent thickener that is soluble in most aromatic, aliphatic and chlorinated hydrocarbon solvents. Soloid is not soluble in methylene chloride."

Soloid was found not to wet with Class I liquids even when vigorously stirred. The material floated on the surface. Class II and Class III liquids gelled extremely quickly. Soloid did not thicken Class IV liquids but tended to swell approximately three times in size.

Soloid was compared with Imbiber beads in gelling isooctane (a Class II liquid). Although the Soloid compound formed a gel very fast, the Soloid powder tended to float on the surface. Mixing was needed to get the powder into the liquid mass, with a noticeable adverse "flour-bag" effect (gelling the exterior surface of masses of agent and rendering the inner material unavailable for reaction). It was found that approximately four times the amount of Imbiber beads compared to Soloid was required to gel isooctane.

Soloid is, therefore, a candidate substitute material for the MGA components for both Class II and Class III liquids.

Kelzan (Kelco Company)--Kelzan is a xanthan gum-polysaccharide which is a thickening agent for Class I liquids. The data sheet obtained shows 1% aqueous solutions to have high viscosities. Kelzan was compared with Gelgard M. When Kelzan was added to water, the powder spread immediately over the surface and formed a surface-gel of sufficient strength to float additional Kelzan on top of the surface. Upon stirring, the powder would agglomerate around the stirrer, producing a large "flour-bag" effect. Approximately twice the volume of Kelzan compared to Gelgard, was needed to gel equal volumes of water. However, the "flour-bag" effect was so great that less than this amount of Kelzan was used in the gelling effort. This product is a potential candidate substitute component in the MGA.

Klucel H and M (Hercules)--Klucel was evaluated as a substitute material for Class IV liquids. A direct comparison was made between Klucel and Carbopol 934. It took approximately twice the amount of Carbopol 934 compared to Klucel to get methanol. Thus, Klucel is a potential substitute component for the MGA.

STORAGE REQUIREMENTS

Samples of the powdered form of the MGA, Blend D, were tested to find the limitations that are imposed upon storage. Containers of MGA were stored from 0 - 100% humidity and from -20 to 104°C (4 to 219°F). These samples were examined weekly for two months and less frequently thereafter.

The MGA stored at room temperature in an open container (relative humidity 50 - 80%) formed a lumpy mass while MGA stored at 100% relative humidity formed a solid spongy mass.

The powdered MGA when stored at high temperature [104°C (219 F)], changed color from white to deep tan in one month, indicating a possible degradation of the organic polymers. Tests on the partially degraded material showed the gelling effectiveness was decreased but not eliminated.

Samples were also stored for six months outdoors, exposed to the elements in containers to evaluate the type of container and the stability of the agent over wide temperature ranges. Fiber drums (Fibre-Pak) manufactured by the Continental Can Company were filled with MGA and placed outdoors in an open unprotected area where they were subjected to the natural environment. The weather over the test period, February through July 1975, was typical of Western New York State. A summary of the general weather over the test period is listed below:

general weather	variable (sunny, rainy, snowy)
temperature	-13.8°C (7°F) to 31.7°C (89°F)
relative humidity	20 to 100%
winds	calm to 35.8 m/sec (80 mph)

The MGA powder stored showed no indication of any deterioration and there was no change in quality when compared to laboratory stored samples. The storage container was not damaged by the weather although there was superficial rusting of the metal parts.

Requirements for storage based on our laboratory evaluations are that the MGA must be stored at temperatures less than 50°C (122°F) and be free from moisture.

PRELIMINARY BIOASSAY

A bioassay screening test was performed to determine the effect of various concentrations of MGA on creek minnows. This particular test was performed to evaluate the consequences of large amounts of MGA washing into a stream or lake. Fish were exposed for 72 hours to 0, 0.01, 0.05, 0.1, 0.5 and 1% MGA (by weight) in water. A 1% solution results in a viscous solution in which the fish could barely swim. The maximum safe concentration was found to be 0.01%. The acute effects of gelling agent were due mainly to the thickening solution which caused suffocation and gelled the fish into the surface layer. After 24-48 hours, MGA precipitated out of solution and remained at the bottom with no effect on surviving fish. Fish exposed to 0.05% MGA solution lost equilibrium from 30 minutes to 24 hours but recovered. The results presented, however, are only preliminary indicators of the toxicity of the MGA upon the water quality when it is used in spill control.

PROCUREMENT AND PHYSICAL SPECIFICATIONS

The physical specifications of the components of the MGA as they were received from their respective manufacturers are listed in Table III-9. Some manufacturers stated that certain information, such as molecular weight distribution, was not available or was proprietary information. The manufacturing specifications, as to type of processing or the type quality control, were classed as proprietary. The generic name of each material is given in Table III-10, but this merely serves as a guide to chemical class since these are polymeric materials and actual manufacturing specifications would have to be used to reproduce the material. Cabosil was the only material for which the generic name and manufacturing specifications would be obtained. This material, a product of the Cabot Corporation, is a fumed silicon dioxide.

TABLE III-8 PHYSICAL PROPERTIES OF WGA COMPONENTS

Trademark	Chem. Class	Used To	Moisture (%)	Spec. Gravity	Heavy Metals	Appearance	Size	Odor
Gelgard	Polyacrylamide	Gel aqueous liquids (e.g. Chlorine H$_2$O)	*	*	-	wh. powder	37% <250 μm	none
Tehiben Beads	Cross-linked alkylstyrene	Gel inert spirits (*-d-cyclo-hexane)	*	1.05	-	wh. sphere	500 μm	none
Carbopol 934	Carboxypoly-methylene	Gel alcoholic (e.g. Methanol)	2	1.41	<10 ppm	wh. dust	5 μm	slight
Hycar 14CC	Precross-linked medium-high nitrile VCR rubber	Gel polar organics (e.g. chlorinated hydrocarbons)	<5	0.98	-	Tan powder	80% <500 μm	pungent
Cabosil	Fumed silicon dioxide	Fluidize the mix and to stiffen the gel	3	0.22 bulk 0.05 flake	<10 ppm heavy metals	wh. flakes	7-14 μm	none

* Not determined

- Trace

TABLE III 10. CLASSIFICATION OF UNIVERSAL GELLING AGENT COMPONENTS

TRADENAME	MANUFACTURER	CHEMICAL CLASS	UTILITY
1. Gelgard	Dow Chemical 2020 Dow Center Midland, Michigan 48640	Water-soluble polyelectrolyte polyacrylamide	Interact with water soluble materials (e.g., chlorine water, formaldehyde)
2. Imbiber Beads	Dow Chemical 2020 Dow Center Midland, Michigan 48640	Polystyrene-butylstyrene copolymerized with divinylbenzene	Interact with nonpolar liquids (e.g., cyclohexane, gasoline fractions, inert spirits)
3. Hycar 1472	B. F. Goodrich Chemical Company 6100 Oak Tree Blvd. Cleveland, Ohio 44131	Polyacrylonitrile-Butadiene copolymer rubber	Interact with strongly polar organic chemicals (e.g., ethylene dichloride, acrylonitrile)
4. Carbopol 934	B. F. Goodrich Chemical Company 6100 Oak Tree Blvd. Cleveland, Ohio 44131	Carboxylpolymethylene polymer	Interact with alcohols, (e.g., methanol, butanol)
5. Cabosil	Cabot Corporation 125 High Street Boston, Mass. 02110	Fumed silica	To fluidize the above mixture and stiffen the gelled mass.

SECTION IV

PHYSICAL FORM OF GELLING AGENT

BACKGROUND

In the early stages of development the MGA consisted of a fine powdery mixture of components described previously. That consistency was selected to provide maximum surface area and thereby achieve maximum speed of reaction with spilled liquids. Early field experiments revealed some disadvantages of the powder form. The most serious was the drift of the fine powder from the target area even under conditions of light to moderate winds (Figure IV-1). In addition, the finest particulates to contact the spilled liquid reacted so quickly that a thin surface film of gel was formed in upper layers which prevented penetration of additional agent into lower layers that had not been affected. Unless sufficient turbulence existed in the stream to provide the necessary mixing of agent with the spilled liquid, flow continued at the lower levels.

It was [illegible]ent from these experiments that the optimum consistency of the gelling agent would be one that preserved the large amount of surface area to promote rapid and complete reaction, and yet contained particles of sufficient size to be relatively unaffected by wind and sink into the volume of the spilled liquid rather than react only with the surface layers. Various techniques for pelletizing and forming loose aggregates of the powder were investigated in an attempt to achieve these results.

It was recognized early in this investigation, which was performed concurrently with investigations of dispersal techniques and equipment, that the utility of a given gelling agent form was in some cases dependent on the dispersal technique used. Since different dispersal equipment may be used for different spills, depending on the size, nature and location of the spill, the objective of this investigation was to select a material form which was usable with the widest variety of potential equipment and which was effective under static conditions without artificial mixing.

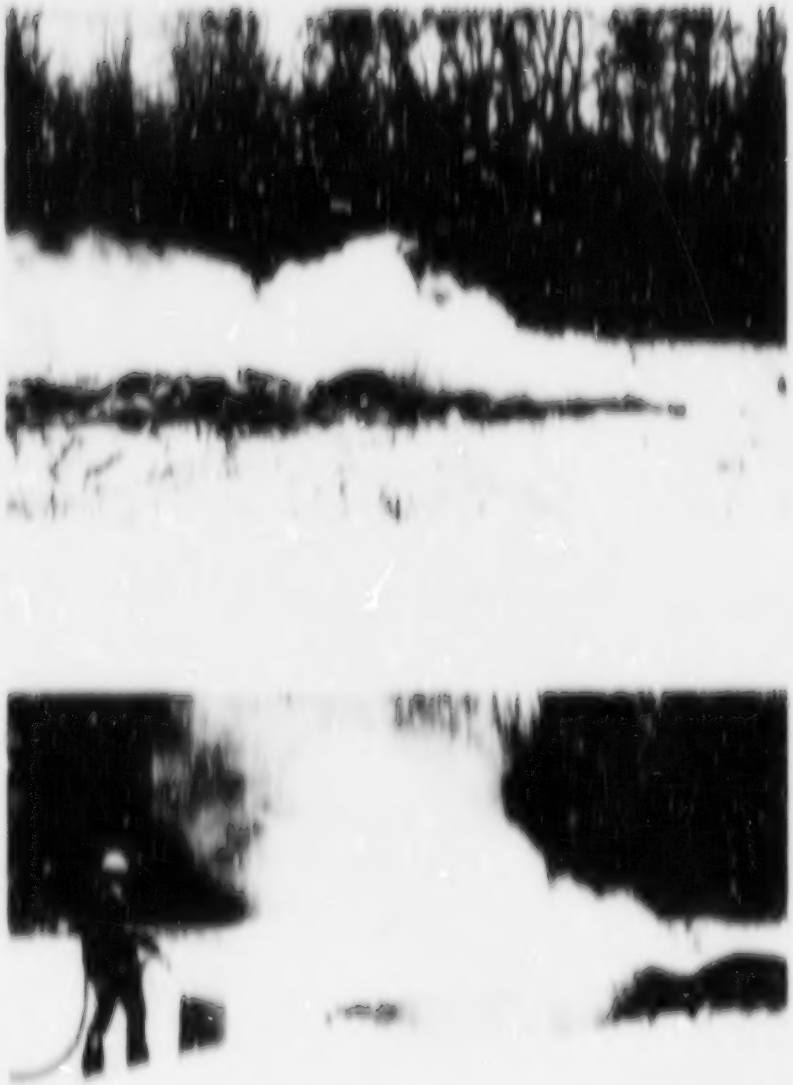

Figure IV-1. Effect of wind on powdered form of MCA being dispersed

OPTIMIZATION OF MGA PHYSICAL FORM

Forms Tested

The material forms included:

(1) The original fine powder;

(2) The powder agglomerated by a water spray;

(3) A variety of tablets;

(4) Crushed tablets that were sieve graded into two mesh ranges;

(5) Webbed, dustless powder;

(6) A mat formed from the webbed powder; and

(7) A roll compressed form chipped into proper sizes.

The standard test procedure used consisted of gently pouring 1.0g of MGA into a vial containing 10 ml of test liquid (the 10:1 gelling ratio) and determining the time required for complete gelation. The criterion for gelation was that no flow should be observed when the vial was gently tipped. When gelation was not observed in this test the experiment was repeated with a doubling of MGA until the liquid was gelled (i.e., 5:1, 2.5:1, 1.25:1 gelling ratio).

Each of the MGA forms was tested against three test liquids from each of the four chemical classes (Table IV-1).

Summary of Test Results

The results of these experiments may be summarized as follows. The "roll compressed" form, produced by chipping the solid layer resulting from roller-mill compression of the powder, and the two "graded" samples, produced by grinding MGA tablets and subsequent sieving for size distribution control, appear to represent the near optimum compromise in material form. These do not react with spilled liquids as quickly as the original powder. However, even under light wind conditions the quantity of MGA reaching the target area may be increased by factors as great as five. These three forms behave well in wind and in some liquids sink slowly through liquid rather than reacting with surface layers only and appear to be useful with all dispersal equipment with which they were tested. However, sufficiently large samples of these forms were not available for testing with all types of equipment.

From the standpoint of ease of manufacture, it appears that the "roll compressed" form has advantages over the other two. On the other hand, the gelling efficiency of the graded forms is slightly superior. The "roll compressed" form and the "graded" forms should be retained as candidate materials for large-scale testing.

TABLE IV-1. TEST LIQUIDS

CLASS I	SATURATED CHLORIDE WATER CONCENTRATED AMMONIUM HYDROXIDE WATER
CLASS II	KEROSENE BENZENE CYCLOHEXANE
CLASS III	O-DICHLOROBENZENE ETHYLENE DICHLORIDE CARBON TETRACHLORIDE
CLASS IV	METHANOL ETHYLENE GLYCOL ISOPROPANOL

The agglomerated form of material performed admirably in the laboratory tests, but was not significantly better than powder in windy conditions. Additional manufacturing costs (which are substantial for this form) are not justified.

The only other acceptable MBA form tested in these experiments was the original powder. Because of problems discussed earlier, however, it must be considered a poor fourth choice.

Results obtained with the materials tested are summarized in Tables IV-2 and IV-3 and discussed briefly in the following paragraphs.

Detailed Test Results

Powder Form--The powder form was obtained by mixing the individual components of the MBA according to the Blend B formulation (5% Gelgard M, 30% Imbiber Beads, 30% Hycar 1422, 25% Carbopol 934, 10% Cabosil). This mixture was most effective in laboratory tests and was used as the control formulation for comparison of gelling efficiency of various forms of MBA.

In most cases, the powdered form gelled the test liquids in less than 10 minutes with a 10:1 gelling ratio (10 ml of liquid to 1.0 g of MBA). However, the alcohols were not gelled satisfactorily. Kerosene, ethylene glycol and isopropanol did not gel even after 60 minutes with the 10:1 gelling ratio. Ratios of 5:1 and 2.5:1 were required to gel these materials. From data presented previously, which were obtained with mixing, it should be expected that these materials should have gelled with the 5:1 gelling ratio. As previously, a large part of the problem in the static experiment was that the initial portion of the powder to contact the test liquid would interact with the liquid to form a protective shell. A "glob" of agent would thus be formed, with the agent in the inner portion of the aggregate remaining dry and not participating in the reaction.

Agglomerate Form--A small batch of MBA (Blend B) was sent to Valentine Laboratories (Clifton, New Jersey) for agglomeration. Particles, 60 mesh in size, were formed by agglomeration with water mist using a GLATT Agglomerator. The bulk density of the agglomerated material was approximately twice that of the powder.

In all but one case, the agglomerated form of the MBA was equal to or better than the powdered form. All liquids gelled within the 10 minutes design parameter, except isopropanol which did not gel. While this form has several advantages over powder, its performance in wind was not a significant improvement. The additional manufacturing expense is, therefore, not justified.

Tablet Form--A variety of tablets of different sizes and physical characteristics was produced from the powder using a disk-making device and a hydraulic press operated in several steps between 5000 and 20,000 psi. Tablet configurations ranging from thin wafers (1-mm thick) to pellets 6 mm (1/4 inch) in diameter and 6 mm (1/4 inch) thick were formed. Most were

TABLE IV-2. EFFICIENCY OF PHYSICAL FORMS OF WGA

TABLE IV 3. GELLING EFFICIENCY OF POWDER MGA (BLEND D & E)

CLASS	TEST LIQUID	POWDER BLEND D		POWDER BLEND E	
		*	**		
I. WATER SOLUBLE	1. SAT. CHLORINE WATER	10/1	0.5	10/1	1.5
	2. CONC. AMMONIUM HYDROXIDE	10/1	7	10/1	1
	3. WATER	10/1	7	10/1	5
II. NON POLAR ORGANICS	1. KEROSENE	5/1	3	5/1	1.5
	2. BENZENE	10/1	0.25	10/1	0.25
	3. CYCLOHEXANE	10/1	4	10/1	2.5
III. POLAR ORGANICS	1. O DICHLORO BENZENE	10/1	0.25	10/1	0.33
	2. ETHYLENE DICHLORIDE	10/1	0.25	10/1	0.25
	3. CARBON TETRACHLORIDE	10/1	1.5	10/1	0.75
IV. ALCOHOLS	1. METHANOL	10/1	7	10/1	8
	2. ETHYLENE GLYCOL	2.5/1	15	5/1	7
	3. ISOPROPANOL	5/1	10	10/1	3

* GELLING RATIO
** MINUTES TO GEL

mechanically stable, i.e., they could be bent or dropped into a hard surface without breaking. However, in all cases the reaction rate of tablets with test liquids was so slow that the concept of using a tablet form of the MGA was abandoned. The experiments with tablet forming techniques were important in that these methods were used as the first step in manufacture of the graded forms of MGA which are very promising.

Graded Form--Large tablets [76 mm (3 inches) in diameter x 3 mm (1/8 inch) thick] of Blend D formed at 6804.6 atm (10,000 psi) were ground into small pieces using a laboratory blender. The ground tablets were then sieved into two fractions (Grade I and Grade II). A photograph of the graded form is shown in Figure IV-2.

Grade I contained a size distribution from 0.25 mm to 1.0 mm. Grade II contained a size distribution of 1.0 mm to 2.0 mm. The particles larger than 2.0 mm were returned to the blender while the finer particles were recycled to the press. The two sieved fractions (Grades I and II) were evaluated separately.

Grade I of MGA was extremely effective in the static tests with 10:1 gelling ratio against all test liquids except kerosene, and isopropanol, for which a 5:1 and 2.5:1 ratio was required respectively. It was also very effective in subsequent field tests against simulated spills. In the latter experiments there were some material losses due to wind but the effect was minor.

Grade II was somewhat disappointing in the static tests, requiring at least a 5:1 gelling ratio for immobilizing seven of the twelve test liquids. In the field tests, however, it appeared to be as effective as Grade I material against the test liquids. Furthermore, there were virtually no wind losses.

On the basis of these experiments we recommend that both Grade I and Grade II material be retained as candidate materials for large-scale field testing.

Webbed Form--The Harshaw process (Harshaw Chemical Company) forms a web of fibers within the powder mixture in order to form a "dustless" powder. The process is as follows: 1% (by weight) Teflon 6 is added to the MGA powder. The material is then mixed thoroughly with the blender and heated for 30 minutes at 103°C (217°F). Fiber formation is initiated by grinding the heated mix with a mortar and pestle. This forms a dough-like material which is then placed in a blender to break it into pieces less than 1 mm in size.

The webbed form of agent is about as effective as the graded forms of the MGA in static tests, but was not very effective in windy conditions, so its further investigation was abandoned.

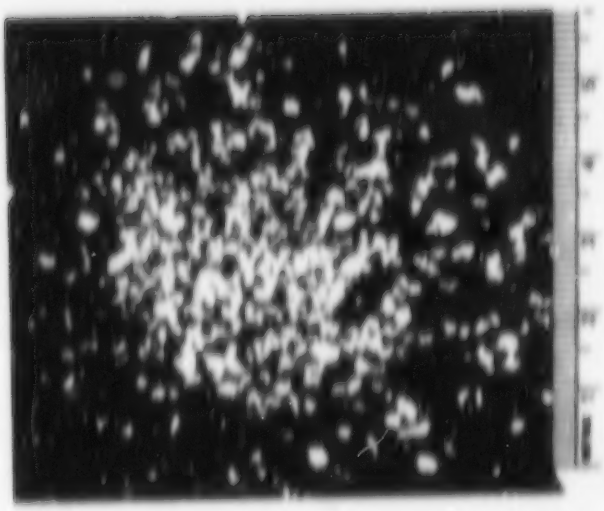

Figure IV 2a. Graded form of MGA.

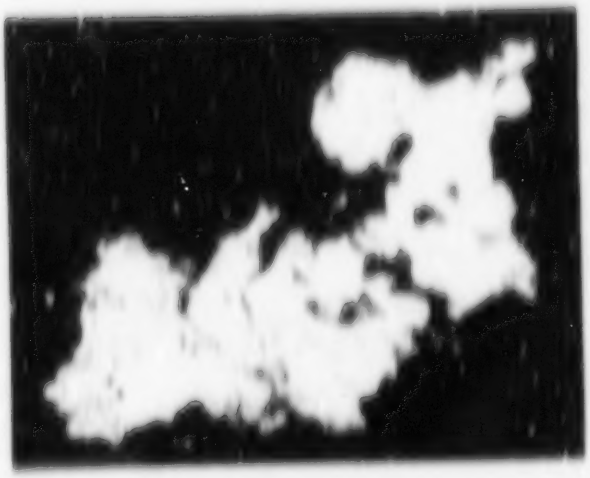

Figure IV 2b. Graded form of MGA (SEM, 20KV, 45° tilt, 80X mag.)

Mat Form-- The mat form was produced by rolling the dough-like mass from the wobbed procedure (above) into a thin sheet approximately 1.6 mm (1/16 inch thick which was then cut into 6-mm (1/4-inch) squares.

Data showed that the mat form did not gel any of the test liquids in less than 45 minutes and its investigation was, therefore, terminated.

Roll Compressed Form--An experimental "production run" of the rolled compressed form of MGA was made by the Valentine Laboratory. A Fitzpatrick compactor was used to produce a continuous sheet of compressed material approximately 1-mm thick which was then chipped into small pieces, 5 mm x 5 mm, with a Fitzpatrick comminutor mill.

As shown in Table IV-2, static tests of this material produced gels in five of the 12 test liquids using 10:1 gelling ratio, one with a 5:1 ratio, five with a 2.5:1 ratio and one with a 1.25:1 ratio. These results are substantially inferior to those obtained with Grades I and II. Three reasons for this decrease in performance can be given. First, the "rolled" form is much more compressed than the tablets from which the graded forms were made. (They are very rubbery in texture and cannot be broken easily or cut except with a sharp knife.) Consequently, the porosity of the "roll compressed" form is low and contact with the liquid is poor. Second, in manufacture of both the "roll compressed" form and the tablets, the outer surface of the MGA is very smooth and has few, if any, pores. In grinding the thick tablets to produce graded forms a large amount of porous surface originally contained within the tablet is produced. However, in chipping the "rolled" form into 5 x 5 x 1 mm chips only a small amount of inner surface is exposed, and approximately half of the total exterior surface of the particles consists of nonporous material that was in contact with the rollers. Again, a substantial reduction in contact of MGA with liquid results. Third, as evidenced by the differences in static performances of Grades I and II MGA ultimate particle size distribution is important. The "roll compressed" material tested consisted of substantially larger particles than either of the graded forms.

Since there is no apparent fundamental difference in the processes used for producing the rolled form and the tablets, it should be possible to manufacture "roll compressed" material which is as efficient as the "graded" forms. This would require 1) reduction of the pressure applied in the roller mill; 2) increasing roller separation to produce a thicker sheet of MGA; and 3) adjusting the comminutor mill to produce smaller particles. These changes in process can be achieved. Unfortunately time restraints prevented another production run during this program.

Because of potential economic advantages of producing the "roll compressed" form of MGA compared with producing the "graded" forms, it should be modified as suggested above and retained as a candidate material for large-scale testing.

Spun Polyolefin Bag Evaluation

Several advantages could be achieved if the MGA could be disseminated in porous bags. Wind drift would be eliminated; retrieval of the MGA-spilled liquid gel would be greatly simplified; manual dissemination for special purposes, such as formation of a dike-perimeter to prevent flow of a spill, could also be simplified.

To test the utility of porous bag packaging, spun polyolefin bags were obtained from Gedcor Environmental Protection Corporation (Westland, Michigan) and filled to half capacity with several of the MGA forms discussed in the previous subsection. The bags were submerged for 10 minutes in one chemical from each class of test liquids and removed for measurement of weight change due to absorbed material. In all cases the quantity of liquid collected was substantially smaller than that gelled in previous experiments with the same agents freely disseminated. Upon examining the bag contents, it was found that reaction of the test liquids with the outer layer of gelling agent had formed a gel that protected the inner portions of the agent from contact with the liquid.

In an attempt to eliminate this "flour-bag" effect, numerous wicking agents (including paper pulp fibers, straw, vermiculite, sawdust and IBM card chips) were mixed with the MGA before packaging, but no significant improvement was observed. Only the "roll compressed" form could be completely wetted and here the reaction rate, apparently limited by a partial "flour-bag" effect, was greatly retarded.

As a result of these simple experiments, the concept of packaging MGA in porous bags for dissemination was abandoned.

SECTION V

DISPERSAL OF THE MOA

BACKGROUND

The Thomas Registry and the on-line computer search facilities at Caispan were used to identify manufacturers of "off-the-shelf" dispersal devices for powders. The search primarily produced agricultural equipment manufacturers. The following companies were contacted for descriptive literature of their equipment:

Buffalo Turbine Agriculture Equipment Company	Gowanda, New York
John Deere	Syracuse, New York
FMC-Agriculture Machinery Division	Jonesboro, Arkansas
Vandermolen Corporation	Livingston, New Jersey
Spraying Systems Company	Wheaton, Illinois
Root-Lovell Corporation	Lowell, Michigan
B. E. Chapin Manufacturing Works Incorporated	Batavia, New York
H. D. Hudson Manufacturing Company	Chicago, Illinois
Standard Container Company	Montclair, New Jersey
International Harvester	Chicago, Illinois
Gehl Company	West Bend, Wisconsin
Mine Safety Appliances Company (MSA)	Pittsburgh, Pennsylvania
U.S. Government	Washington, D.C.

Table V-1 lists the information available on the dispersal devices.

TABLE V-1. DISPERSION DEVICES

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

In general, liquid-carrier systems have replaced dry-chemical dispersal systems. The agricultural blowers which direct powder via a nozzle or exit tube are no longer in production. They have been replaced with blower systems which disperse powder into the air forming a large dust cloud. The equipment is used for agricultural orchard dusting.

There are two systems used in the mining industry that disperse lime dust as a dry powder over the walls and floor of the mine shaft in order to eliminate underground explosions. One system consists of a hopper loaded, auger fed, pneumatic conveyor. This unit transports the powder, at approximately 3.6 to 4.5 kg (8 to 10 pounds) per minute, through a 51-mm (2-inch) diameter hose for distances up to 50 meters (200 feet). The other system used is a pressurized tank which holds up to 2.7 long tons (3 short tons) [2.5 cubic meters (88 cubic feet)] of lime dust. The pressurized tank delivers 0.19 cubic meter (6.6 cubic feet) of lime per minute through a 30-meter (100-foot), 51-mm (2-inch) diameter hose. The system is pressurized with a 5.82 cu m/min (155 cfm)/3.58 atm (38 psi) air compressor.

In addition to the investigation of devices for delivering bulk material to spills, a brief evaluation was made of devices for dispersing canisters and containers. These devices were considered for air-dropping MOA onto spills that were otherwise inaccessible. In principle, the canisters would spread the MOA over the target.

DISSEMINATION SYSTEM EVALUATION

Four dispersion systems were evaluated: (1) a pressurized tank, (2) a Venturi/compressed air, (3) a centrifugal blower, and (4) an auger-fed/pneumatic conveyor.

System evaluations were performed using powder agglomerate, Grade I, Grade II and Rolled forms of MOA. The effect of wind, amount of MOA arriving at target, dispersal pattern, and ease of dispersion were measured.

Pressurized Tank

A rechargable CO_2-charged dry chemical fire extinguisher was used to evaluate the pressurized tank concept. An Ansul Company (Marinette, Wisconsin) Model A-1-C fire extinguisher was loaded with approximately 0.22 kg (1/2 lb) of MOA, sealed and charged with a CO_2 cartridge.

The nozzle configuration of the test equipment used was designed for discharging a fine powder for extinguishing fires and the larger MOA forms (Grade II and Rolled) plugged the nozzle. However, with a properly designed nozzle size, the larger size particles of MOA could be used.

A stainless steel tray [61 x 76 x 5 cm (24 x 30 x 2 inches)] was used to collect the MOA that settled on the simulated spill target. The distance between the nozzle and the simulated target was selected so that the maximum amount of MOA would remain at the target site. Results were as follows:

Powdered:--Less than 10% of the powdered MIA was collected in the simulated target. A detailed study of the mass distribution of MIA components settled from the plume under zero wind conditions is presented in a later subsection. The plume was wide and long. Even in light wind [107 to 214 m/min (4 to 8 mph)] most of the powder blew away from the target area.

Agglomerate:--Less than 30% of the MIA hit the simulated liquid spill target. The plume was not as large as the powdered MIA; however, there was still considerable dispersal due to wind.

Grade I:--Approximately 50% of the MIA was collected on the simulated liquid spill target. The plume was much smaller than the other plumes and covered the target area.

Grade II:--The material was too large to permit expulsion from the nozzle.

Roll Compressed:--The material was too large to permit expulsion from the nozzle.

These initial experiments demonstrated very vividly the importance of maximizing the mass to aerodynamic drag ratio of the MIA. In addition, they demonstrated that the pressurized tank method of dispersion can be considered a candidate system if a large reservoir is used with an air compressor. The reservoir could be, for example, a tank approximately 2 meters (6 feet) in diameter and 5 meters (15 feet) long, located on a truck or trailer bed that is also equipped with a gasoline-powered air compressor. In this configuration, assuming that the tank was 3/4 full of MIA, the tank would hold approximately 2268 kg (5000 lb) of powdered MIA. This type delivery system is commercially available from Mine Safety Appliance (Pittsburgh, Pennsylvania).

A possible disadvantage of this system is that when operated with an ambient air compressor, condensation produced by expansion between the tank and nozzle, or perhaps within the reservoir could react with the agent and prevent proper dispersal. Additional tests are required with a large size unit.

Venturi/Compressed Air

To evaluate this type of system, an Econo-Vac sandblasting unit (Airplaco, Clipper Manufacturing Company, Kansas City, Mo.-Model EV-10M) was used with an Ingersoll-Rand 085 gasoline-driven air compressor (Figure V-1).

A 5.6-liter (1-1/2-gallon) spill of trichloroethane was used as a test spill. The exit nozzle was held approximately 60 cm (2 ft) from the liquid surface. Various forms of MIA were evaluated.

Figure V-1a. Venturi tube – compressed air nozzle.

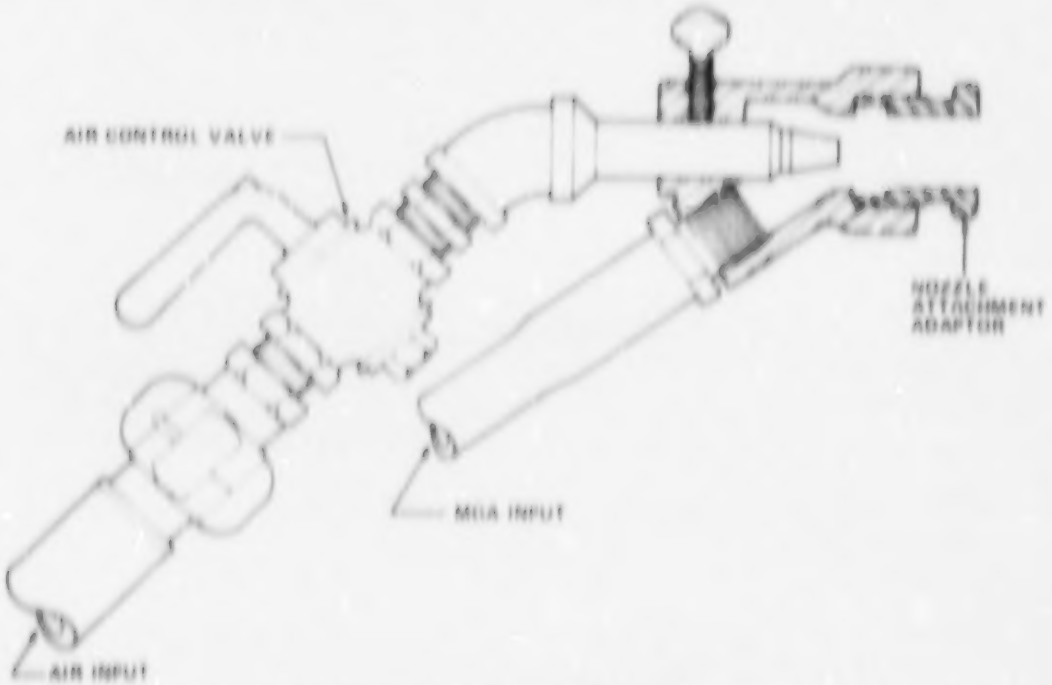

Figure V-1b. Diagram of Airplace Econo-vac nozzle.

Powder--Wind, as well as the volume of air from the sandblasting unit, caused considerable amounts of MMA to be blown away from the target. It took approximately 2 minutes of dispersion to gel the liquid into a gelatinous but not solidified mass. The mixture would slowly flow when the tray was tipped (Figure V-2).

The Econo-Vac sandblaster delivered approximately 1.5 kg (3-1/2 lb) of powdered MMA per minute with the Venturi feed tube placed directly into a fiber drum of MMA.

Agglomerate--The air from the sandblaster caused considerable mixing action of the MMA with the liquid spill when the straight non-flexible exit nozzle was used. This form of MMA gelled the trichloroethane into a solid mass in 30 seconds, which did not flow even when the tray was inverted (Figure V-3).

Grade I & II --Both could be effectively dispersed with this type of delivery system. The larger particles (Grade II) were least affected by the wind but both performed well. Both grades produced an excellent gel with approximately the same amount of material.

Rolled Compressed-- This was the optimum physical form for this dispersion system. The material could be dispersed approximately 6 m (20 feet) without adverse wind effects. During the evaluation, the MMA mixed well with the 5.6-liter (1-1/2 gallon) test liquid spill (trichloroethane) and gelled it in minimal time.

This system of dispersion is flexible and commercially available. It is a definite mode of dispersion for all the forms of multipurpose gelling agent tested.

Centrifugal Blower

To evaluate this mode of dispersion, a snowblower (Ariens, 5 hp) was used. The snowblower was tipped so that the screw-fed hopper was facing up allowing the MMA to be poured directly into the blower. The centrifugal blower blew the MMA into the air over the liquid spill target. The wind effect on this system is severe using both powder and agglomerate forms of MMA (Figure V-4). Less than 10% of the powder and 20% of the agglomerate landed on a 6 x 6 m (20 x 20-foot) target even though the wind conditions were near calm [maximum gusts were 134 m/min (5 mph)]. This dispersion mode has, therefore, been eliminated as a possible delivery system.

Auger-Fed/Pneumatic Conveyor

A Bantam 400 Rockduster (Mine Safety Appliances Company, Pittsburgh, Pennsylvania) was used to evaluate this mode of dispersion. The Rockduster consisted of a hopper which auger-feeds the MMA to a moving air stream. The volume of air is varied depending on the density of the material being dispersed. This unit can transport the powder through a 5-cm (2-inch) ID hose up to 60 m (200 feet) long.

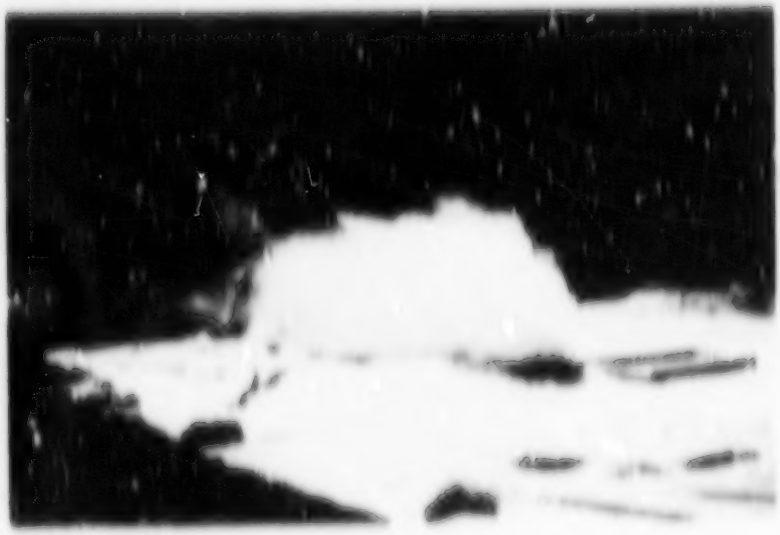

Figure V.2. Venturi compressed air system blowing powdered form MQA.

a. DISPERSING AGGLOMERATED FOAM

b. GELLED TRICHLOROETHANE

Figure V 3. Long tube on Venturi compressor

a. EXPERIMENTAL APPARATUS

b. BLOWING POWDERED MGA

Figure V-4 Centrifugal blower (snowblower)

The hopper was filled with approximately 0.05 cubic meter (2 cubic feet) of powdered MGIA and used a 30 m (100-foot) section of exit hose. This configuration delivered 3.6 kg (8 lb) of MGIA per minute with less than 20% loss due to wind (Figure V-5).

The unit as manufactured is driven either by a 3.7-kW (5-hp) electrical unit (440 or 220 volts DC) or by a hydraulic unit [0.7 l/sec at 60 atm (12 gpm at 1000 psi)]. Neither of these modes of power is ideal for portable field application, but the unit can be modified to use a 120 volt AC motor or a gas-driven motor. This unit is the most promising off-the-shelf equipment tested.

Nozzle Configuration

Several experiments were also performed to evaluate possible nozzle configurations that might be used with these systems. The Venturi tube system equipped with a 4.4-cm (1-3/4-inch), 3-m (10-foot)-long exit tube was used.

Best results were achieved using a 4.4-cm (1-3/4-inch) diameter tube that had been bent at an angle of 30° to the exit tube. This simple device permitted the operator to accurately direct the plume of the MGIA at the region of the spill he wished to treat. Directing the plume down caused the plume to strike the spilled liquid at relatively high velocities, thereby minimizing wind drift of powder and, more importantly, causing substantial agitation of the liquid as the agent entered it. This agitation promoted rapid and complete reaction of the agent with the liquid.

Other configurations tested included a deflection plate, a nozzle with an expanded opening and, of course, the straight pipe. These configurations were substantially less effective in permitting accurate placement of the plume.

Mass Distribution of Powdered MGIA

The mass dirpersion of the powdered form of MGIA was evaluated indoors to eliminate the adverse effect of wind.

MGIA was placed in a CO_2-charged dry chemical fire extinguisher whose nozzle was collimated with a 1.2 cm (1/2-inch) diameter tube, 50 cm (20 inches) long. The nozzle was pointed at a target 2.4 m (8 feet) away and the entire amount of MGIA was discharged in several short blasts.

A collection grid system consisting of petri dishes was used. After expulsion, the amount of gelling agent collected in each dish was determined. The distribution profile is shown in Figure V-6. The outer line in Figure V-6 shows to what extent the finer materials of the blend drifted and contour lines illustrate equal mass distributions. Seventy-five percent of the material dispersed was collected within the target area (broken line).

In order to determine the distribution of each MGIA component another discharge of universal gelling agent was performed. In this experiment, the collection grid consisted of the petri dishes set at one foot intervals in a

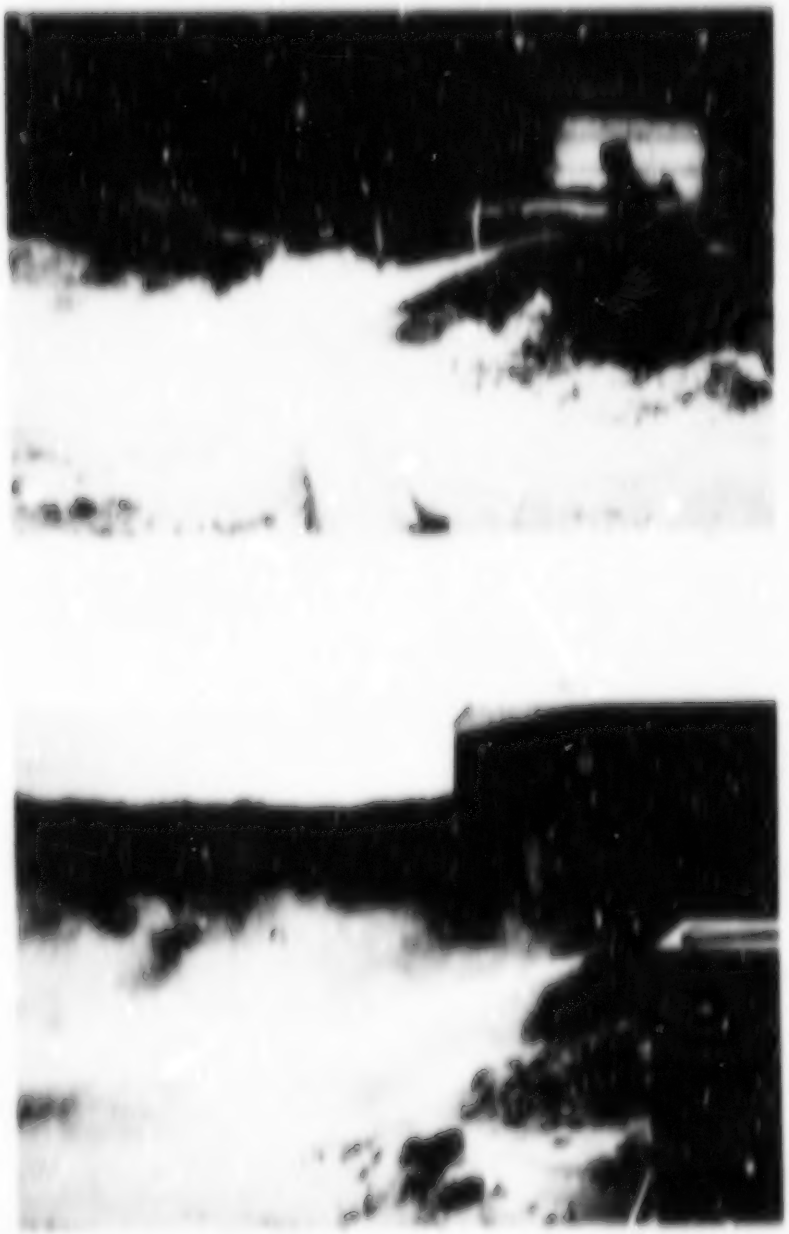

Figure V 5. MGA dispersed from pneumatic conveyor/auger fed system. Powdered MGA being dispersed from 30 meter (100 foot) hose.

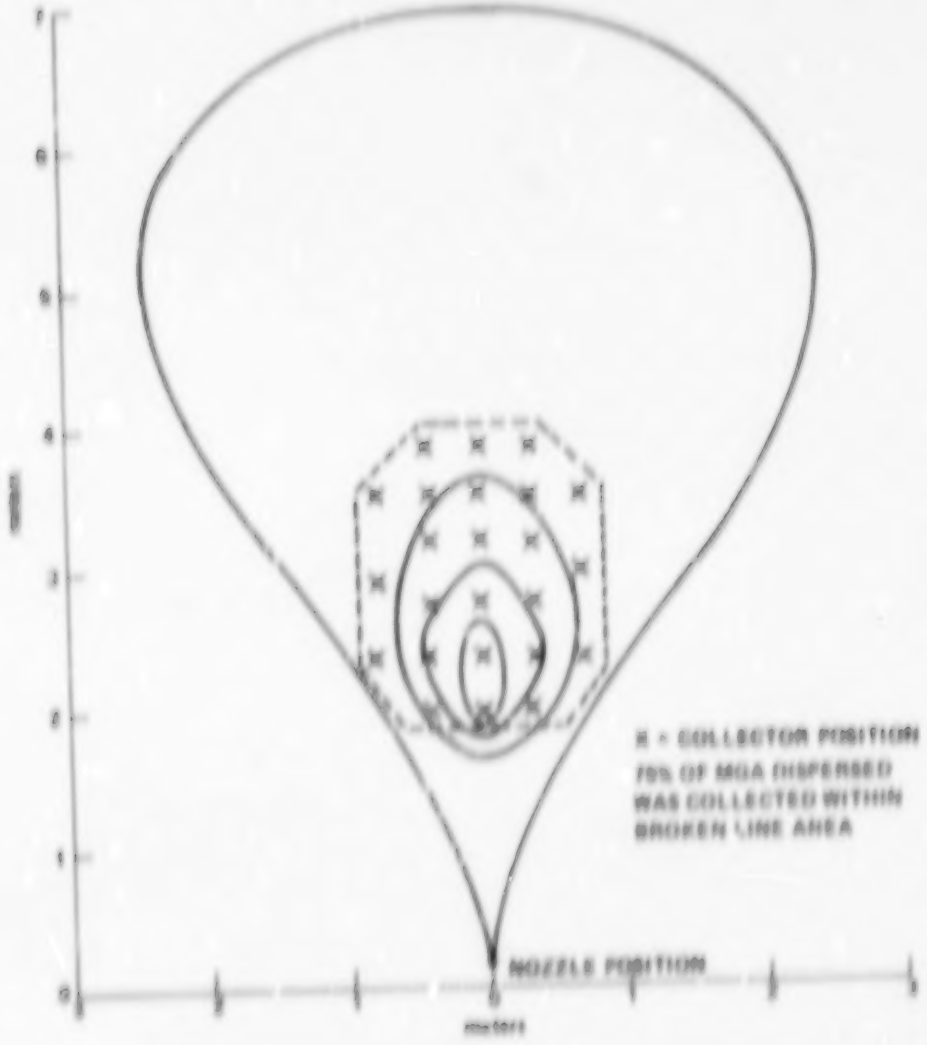

Figure V-6. Equal mass distribution contour map obtained from CO_2 charged dry chemical fire extinguisher dispersion of MGA.

linear array. The nozzle was held in a horizontal position approximately three feet above ground. The MIA was again discharged from a CO_2 dry chemical fire extinguisher.

The dispersion distribution characteristics were determined by viewing each collection dish with a light microscope at low magnification (40x). Each MIA component showed a dispersion pattern that was predictable using its density and particle size. The dispersion characteristic of each component is as follows:

Geigard--The Geigard is of an irregular shape and has the appearance of gravel. The distribution peaked around 2 meters from the nozzle with no material dispersed beyond 5 meters.

Imbiber Beads--The distribution of these spherical-shaped beads peaked at 0.75 to 1 meter and beads were only seen sparingly beyond 2 meters.

Hycar 1422--This material is also spherical but only 1/5 the diameter of the Imbiber Beads. Its distribution also peaked at 0.75 to 1 meter, declining rapidly at 3 meters. Unlike Imbiber Beads, it was readily seen over the entire collection grid.

Carbopol 934--This component has the appearance of a very fine powder and is adsorbed to the Geigard, Imbiber Beads and the Hycar 1422; it was found to be dispersed over the entire pattern.

Cabosil--The Cabosil consists of very fine, irregular, transparent pieces. Their distribution was observed over the entire collection grid but was mainly found beyond the 2 meter mark.

The mass distribution of the total mixture peaked at 5 meters with a half width of 1 meter (Figure V-7).

This experiment revealed a particularly important disadvantage of the powdered form of MIA, i.e., separation of components with distance from the nozzle. (This separation cannot occur with any form tested except powder.) It is apparent that, if the powdered form of MIA is used on real spills, a nozzle configuration which permits direct impaction of the plume on the liquid is essential.

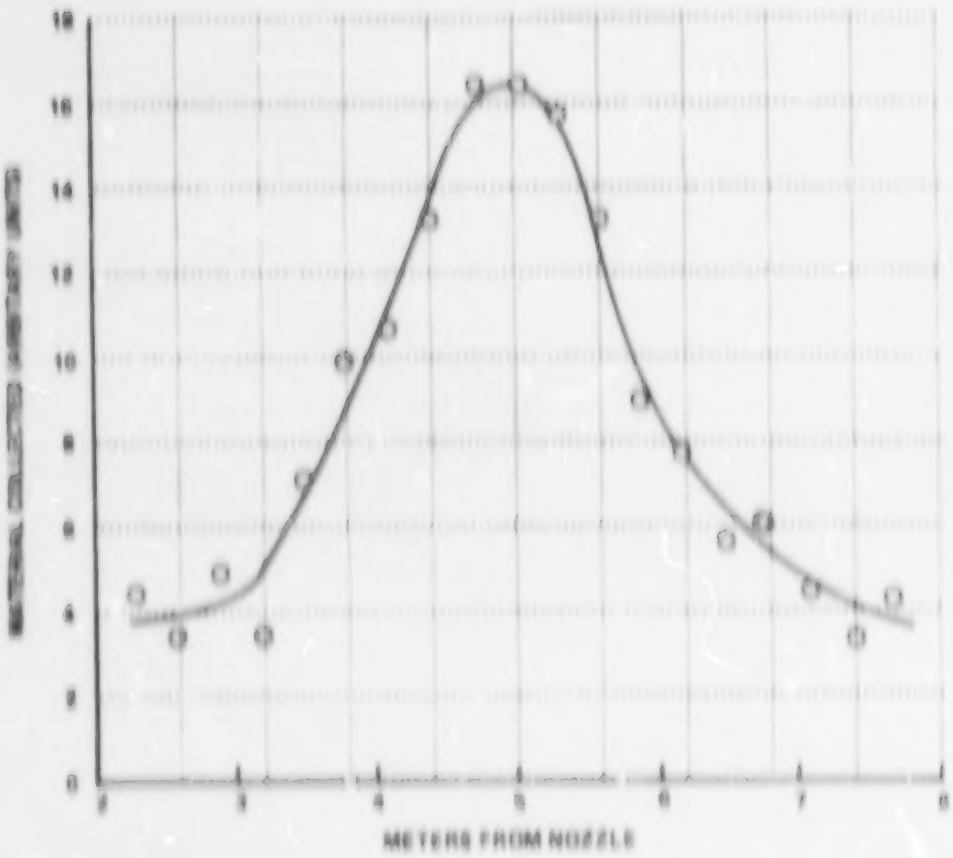

Figure V-7. Mass distribution of MGA dispersed from CO_2 charged dry chemical fire extinguisher.

SECTION VI

DISCUSSION

Efforts to optimize the gelling agent blend produced clear cut results. Blend D, consisting of Geigard M, Imbiber Beads, Hycar 1422, Carbopol 934 and Cabosil, is substantially superior to other blends of the original materials tested. Blend E, in which Klucel H was substituted for Carbopol 934 in Blend D, showed slightly superior performance on the alcohols. However, since no experience was obtained in the manufacture of optimum forms of Blend E, we believe that Blend D should be retained as the prime candidate for large-scale experiments. Tests also showed that "kelzan" can be substituted for Geigard and Soloid for Imbiber Beads without seriously affecting performance. Since manufacturers of the four components of Blend D occasionally remove and substitute items in their product lines it would be wise to perform simple experiments by the manufacturing of selected MeOA forms using substitute materials in anticipation of the possible elimination of one of the components from the market.

The experiments with different physical forms of MeOA produced clear evidence that the "agglomerate" form and "graded" forms were superior to all others in static tests. However, the "agglomerate" form can be eliminated on the basis of its poor performance in wind and its high manufacturing costs. Grade I was superior to Grade II in the static tests but inferior to Grade II in wind. The smaller particles in Grade I, i.e., 250 μm to +500 μm, were subject to significant wind drift, while the larger particles in Grade II gelled slowly. The latter effect is not necessarily a disadvantage in treating real spills, since the larger particles sink more rapidly into a spill to react with the volume of liquid rather than the upper surface.

We believe, therefore, that the optimum "graded" form should consist of particles between 0.5 and 2 mm. This material can be produced by the same manufacturing techniques used during this program (exercising proper selection of sieve mesh).

The "roll compressed" form used on this program was inferior to the "graded" forms in static tests, but performed well in the field. As discussed in the text, the reasons for the reduction in performance are understood and can very probably be corrected by slight adjustments in manufacturing procedures. Because of potential economic advantages of these manufacturing procedures, we recommend that the "roll compressed" form be retained for testing in large-scale experiments.

Three kinds of off-the-shelf equipment proved to be useful in the small-scale field experiments performed on this program. These include:

(1) Pressurized tanks similar to equipment manufactured by Mine Safety Appliances, Company of Pittsburgh, Pennsylvania;

(2) Venturi/compressed-air types manufactured for sandblasting purposes; and

(3) Auger-fed, pneumatic-conveyor equipment similar to the "Rockduster," also manufactured by Mine Safety Appliances.

The "Rockduster" appears to be most suitable for treatment of large spills. Because of costs and the difficulty in transporting this equipment, it is probably suitable for distribution only with large stockpiles of gelling agent. Less expensive, easily transportable type equipment, such as sandblasters, would be more appropriate for distribution with smaller local supplies of the agent, such as at firehouses.

All three forms should be retained as candidates for large-scale testing.

Any of these units can be used with straight pipe nozzles or nozzles in which the exit tube is bent at approximately 30°. Large-scale tests should be performed with straight pipes equipped with detachable extensions bent at 30°.